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MECHANISMS AND KINETICS OF COAL HYDROGENATION

Quarterly Progress Report for October—December 1979

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MECHANISMS AND KINETICS OF COAL HYDROGENATION

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OBJECTIVE AND SCOPE OF WORK

Colorado School of Mines is conducting coal hydrogenation research with the following objectives and scope of work:

1. Comparison of the rates of coal hydrogenation in continuous flow stirred tank and tube flow reactors using pure hydrogen, catalyzed CO-STEAM, and syngas processing conditions.
2. Investigation of the influence of coal rank on the rate of hydrogenation of coal to preasphaltenes, asphaltenes, and oil in batch reactors.
3. Batch evaluation of the effect of operating conditions (temperature and pressure) on the rate of hydrogenation of coal-derived preasphaltenes and asphaltenes.
4. Determination of the effect of selected disposable catalysts on the rate of batch hydrogenation of preasphaltenes and asphaltenes and selected bituminous coals. Testing and evaluation of promising catalyst systems in the continuous processing unit.
5. Formulation of a unified kinetic/mechanistic model for coal liquefaction taking into account petrography of the feed coal and hydrocarbon lumps in the product oil.

Task I Milestone Chart

Task II Milestone Chart

TASK I

CONTINUOUS PROCESSING STUDIES

The objective of this task is to compare and evaluate the rates of coal hydrogenation in the Colorado School of Mines Continuous Processing Unit using two reactor configurations (stirred tank and tube-flow) and three gas processing conditions (pure hydrogen, CO-STEAM, and syngas). Engineering correlations for coal hydrogenation rates will be developed showing the expected effects of temperature, pressure, coal rank, reaction atmosphere gas, and reactor configuration. The task will be performed using the bench-scale, single-pass continuous hydrogenation unit developed and tested under DOE Contract No. EX-76-C-01-2047.

This task is inactive awaiting completion of project staffing.

TASK II

COAL REACTIVITY STUDY

The objective of this investigation is to determine the effect of coal physical and chemical properties upon the rate of coal hydrogenation to primary products such as preasphaltenes, asphaltenes, and oils. Responses measured will be the rate of disappearance of reactive coal macerals and rate of formation of preasphaltenes, asphaltenes and oils. Models will be developed attempting to incorporate parent coal petrographic composition, as well as gross hydrocarbon species in the liquid product.

During the past quarter effort has been directed toward selection of coals to be tested, construction of the experimental apparatus, and initial testing of the apparatus.

Coals have been selected from the Penn State Coal Sample bank using the following selection criteria:

1. bituminous coals
2. less than 5 wt % pyrite content
3. widely variable maceral content
4. widespread geographical distribution.

Thirteen coals were chosen for the bituminous coal portion of this study; these coals are listed in Table I.

The experimental apparatus is similar to batch equipment used in earlier studies at this institution, with modifications to permit sampling of reactor contents (solids and liquids) during experiments, see Figure 1.

Figure 1: Experimental Apparatus, Coal Reactivity Study

The reactor is a one-liter, batch, stirred reactor manufactured by Autoclave Engineers. The system is designed to insure rapid coal injection into the system using high pressure hydrogen to force a small amount of concentrated slurry from a small storage vessel into the reactor. Samples are withdrawn from the reactor using a diptube through the reactor head.

Shakedown Test on Sampling System

Late in the quarter, a test run on the reactor system was made in order to verify the feasibility of the reactor design modifications described above. The points to be verified were:

1. The amount of sample coal which is held up in the injection system should be small.
2. The samples of solvent-coal slurry taken from the reactor system should be representative of the material in the reactor.
3. All the coal recovered from the samples, slop, reactor vessel and the injection system should reflect an accurate accounting of the amount of coal initially weighed out.

The test was performed on an unknown coal, ground to -200 mesh. Tetralin was used for the slurrying fluid and the test was run at room temperature under approximately 1800 psig of helium.

A tetralin:coal mixture in a 2:1 weight ratio was prepared from 70.21 g of tetralin and 35.41 g of coal. This was injected through the top port of vessel, C1. Precisely 3.46 g of material clung to the syringe, beaker, paper towels, etc. which were used in the process of charging the sample to C1. This uninjected material appeared to be predominantly coal, but some tetralin must be presumed to have been part of the unrecovered

material. This was the only uncertain aspect of the mass balance. Two limiting assumptions with regard to this uncertainty will be made in the latter part of this discussion. These are:

1. All of the unrecovered material was coal.
2. The material was a coal:tetralin mixture of the same ratio as the slurry.

These assumptions should bracket the real case and are, thus, presumed to be limiting cases.

388.12 g of tetralin were initially charged to the reactor vessel. The vessel was then pressurized to 900 psig of helium. After the coal slurry was placed in C1 all the sample injection fittings were resealed and the lines were leak tested at 1800 psig of helium.

With container C1 pressurized to 1800 psig with He, valve V5 was opened. This created a 900 psi pressure differential between C1 and the reaction vessel which forced the coal slurry into the reactor. The tetralin in the reactor had been stirring at 1500 rpm for an hour prior to injection. The slurry mixture was allowed to settle for almost an hour in C1 prior to injection. This was done to simulate a "worst case" situation with respect to potential plugging of the 1/8 inch line which connects C1 with V5. No problems with plugging of the line were observed.

Samples of the test mixture were taken by cracking valve V4, closing V4, and then opening V1 on the "slop" side to rinse the diptube and the line between V1 and V4 with slurry. The same procedure was then immediately repeated, except that the "sample" side of the three-way valve, V1, was opened the second time. This yielded a sample of approximately 3.5 g in

in mass. The entire procedure took approximately 10 seconds, a short enough period to assure little risk of loss of sample integrity due to temporal changes.

Samples were taken from the reactor at times of 1, 5, 10, 30 and 60 minutes after injection. After the last sample had been taken, the reactor stirrer was shut off and the reactor depressurized. The reactor, the sampling system (between V4 and the outlet lines of V1), and the storage-tank system (between V2, V3 and V5) were carefully washed with acetone to collect all of the coal which remained in them. These three washes, along with the slop sample and the five timed "samples" were each washed three times with acetone (to remove the non-volatile tetralin) with centrifugation and decantation of the acetone between washings. The samples were then dried overnight at 37°C until free of acetone. The vessels had been pre-tared so that the weight of recovered coal from each of the reactor areas and from the samples could be calculated. The distribution was as follows:

<u>Sample</u>	<u>Sample Mass (g)</u>
Storage Tank	2.43
Sampling System	0.15
Reactor	29.25
Slop Samples	0.77
1 min. sample	0.2020
5 min. sample	0.1981
10 min. sample	0.2017
30 min. sample	0.2178
60 min. sample	<u>0.2060</u>
total	33.63 g

The timed "samples" were weighed prior to the acetone washing so that the percentage of coal in each of the slurry samples could be determined. The weight of slurry in each sample and the percent coal calculated for each is given below:

<u>Sample</u>	<u>Slurry Collected</u>	<u>wt. % coal in sample *</u>
"slop" sample	12.76	6.03
1 min. sample	3.4921	5.78
5 min. sample	3.1808	6.23
10 min. sample	3.4331	5.88
30 min. sample	3.5568	6.12
60 min. sample	3.1931	6.45

As mentioned above, there are two limiting-case assumptions which can be made regarding the uninjected slurry mixture. One of these assumptions must be made in order to complete the coal mass balance on the system. Each case is considered below.

1st Case:

In this case, it is assumed that all 3.46 g of material which clung to the injecting apparatus was coal. By this assumption, the only part of the original coal/tetralin slurry which didn't reach the reactor vessel is assumed to be the 3.46 g of unrecovered coal plus the coal:tetralin, 1:2 slurry which remained in the holding tank, C1.

* Example Calculation, 1 minute sample:

$$\frac{\text{wt. coal in sample}}{\text{wt. slurry collected}} \times 100 = \% \text{ coal in sample}$$

$$\frac{0.2020 \text{ g}}{3.4921 \text{ g}} \times 100 = 5.78 \% \text{ coal in 1 min. sample}$$

2nd Case:

In this case it is assumed that the 3.46 g of unrecovered material was coal and tetralin in a 1:2 ratio. The same assumption is made for the material remaining in C1, as was assumed in Case 1.

Calculation of slurry mix:

The fraction of coal in the slurry mixture is:

$$\frac{35.41 \text{ g coal}}{35.41 \text{ g coal} + 70.21 \text{ g tetr.}} = 0.3353 \text{ (g coal/g slurry)}$$

The ratio of solvent to coal is:

$$(70.21 \text{ g tetr.}) / (35.41 \text{ g coal}) = 1.983$$

These values are needed for the calculation of the mass balances given in Table 2, which follows.

TABLE 2:

Mass Balances on Coal for Sampling and Injection System Tests

COAL TO REACTOR:

	<u>CASE 1</u>	<u>CASE 2</u>
initial	35.41	35.41
-uninjected	-3.46	(.3353x3.46) -1.16
<u>-left in C1</u>	<u>-2.43</u>	<u>-2.43</u>
coal in reactor (calculated)	29.52	31.82

TETRALIN TO REACTOR:

initial	388.12	388.12
+prep'd w/slurry	70.21	70.21
-uninjected tetralin	N/A	(0.6647x3.46) -2.30
<u>-remaining in C1</u>	<u>(1.983x2.43) -4.82</u>	<u>(1.983x2.43) -4.82</u>
tetralin in reactor	453.51	451.21
% coal in reactor	6.11%	6.59%

These test results were satisfactory on all three of the points which were mentioned at the beginning of this Appendix.

Point 1: The amount of coal held up in the storage vessel (C1) was 2.43 grams. This amounts to only 7% of the coal which was initially weighed out for the experiment. 31.20 grams of coal were recovered, in total, from the reactor, sampling system, and the "samples". This implies that 88% ($31.20/35.41$) of the coal that was weighed out initially reached the reactor system. This is satisfactory for the experimentation at hand.

Point 2: The percentage of coal in the reactor was calculated to be between the two limiting cases, 6.11% and 6.59%. Nearly all the samples fell within this range (3 of 5). Within the margin of error for the washing/drying methods used on the samples, the samples can be considered to be representative of the mixture which was in the reactor. The two samples which fell below the expected coal percentages may be explained by the expectation of a certain amount of dissolution of the coal (or suspension of the smaller particles) in the acetone or the partial volatilization of the coal during drying.

The percentage of coal in the 1 minute sample was lower than may have been anticipated (5.78%). This could be an indication of incomplete mixing of the injected slurry with the solvent in the reactor at the early stages of reaction.

Point 3: As mentioned in Point 1, the sum of the coal recovered from the reactor, sampling system, and the samples amounted to 31.20 grams of coal. By the two cases used as limiting assumptions, the amount of coal which reached the reactor should have been between 29.52 and 31.82 grams.

31.20 grams is bracketed by these limiting values.* With a more careful accounting of the slurry which does not reach the injection system, mass balances accurate to one or two percent should be feasible.

During the next quarter tests will continue to determine if any plugging problems will exist in the sampling diptube at reaction temperature. A final determination of analytical tests to be used will be made. If the feasibility tests are successful the actual experimental program will be started.

Disposable Catalysts and Coal Mineral Matter

The objective of this study is to determine the influence of disposable catalysts and coal mineral matter upon the rate of hydrogenation of selected coals, and upon the rates of hydrogenation of products such as preasphaltenes and asphaltenes.

The initial investigation in this area will be a series of screening tests using disposable catalysts and coal. The catalysts to be investigated are FeS , Fe_2O_3 , molybdenum ore, molybdenum tailing, and coal mineral matter. The study will be carried out using a reactor system comparable to that shown in Figure 1 with a 300 ml reactor.

During the past quarter construction of the experimental apparatus was started. During the next reporting period construction will be completed and initial testing begun.

* Note: These figures imply that the Case 2 assumption (ie. unrecovered material was 2:1, solvent:coal) is closer to actuality than was Case 1.